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(54) Title: THIN FILMS OF CORE-SHELL NANOPARTICLES (57) Abstract The present invention relates to the preparation of thin films from inorganic particles with sizes of the order of 1-100 nm, on which a layer of a different inorganic or high molecular weight organic material is deposited. The deposited shell is responsible for a definite change in the properties of the core material within the thin film and for the applicability of the material to the preparation of various types of devices.		

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THIN FILMS OF CORE-SHELL NANOPARTICLES

BACKGROUND OF THE INVENTION

1. Field of the Invention:

This invention relates generally to thin films of inorganic nanoparticles, and, more specifically, to thin films of core-shell nanoparticles wherein the core and shell comprise different materials. In a preferred embodiment, the invention relates to the preparation of thin films from silica-coated magnetic nanoparticles.

2. Background of the Invention:

Thin film technology, wherein inorganic particles with sizes on the order of 1-100 nm are arranged in layers to form a film, is being used presently for an increasingly large number of different technological applications, including, among other things, information storage systems, chemical and biological sensors, fiber-optical systems, magneto-optical and optical devices, pervaporation membranes, protective coatings and light emitting diodes. Current techniques for preparing such films include chemical vapor deposition (in which no discrete inorganic particles are involved), sol-gel technology (producing porous materials that can be sintered to get uniform films), or deposition from colloidal dispersions (spin-coating, dip-coating, Langmuir-Blodgett deposition, etc.).

Thin films of nanoparticles as presently constructed have a limited effective lifetime due to the fact that the nanoparticles may be relatively unstable in air. Using any of these techniques, it is also often difficult to preserve the properties of individual nanoparticles during film formation, since there can always be a certain degree of contact between neighboring nanoparticles. This may result in a change in the optical or electronic properties of the particles and resulting film, rendering the film useless for its intended purpose.

It is thus an object of the present invention to provide a thin film of nanoparticles wherein the property of interest of the nanoparticles is preserved and wherein the individual nanoparticles are isolated with respect to each other and with respect to their exposure to the environment.

It is a further object to enable the enhancement of properties of nanoparticles and impart new properties to particulate assemblies of nanoparticles via controlled interparticle interaction.

In a particular application, namely the technology of information storage systems and magnetic recording, a qualitative modification is required when surface densities of hard disk drives approach 1.5 Gbit/cm². The reduction of the bit dimensions require a decrease of the grain size to keep a suitable signal-to-noise ratio. When the anisotropic energy, which is proportional to the particle volume, of the small magnetic domains becomes comparable to their thermal energy, which is defined as superparamagnetic limit, the thermal energy at T=300 K can destabilize the stored bit, causing loss of data.

The accuracy of the spatial discrimination of magnetic domains in magnetic storage media depends on the coupled magnetization flipping in adjacent grains. The grain size in top-of-the-line hard drives which use continuous magnetic materials is already as small as 10 nm and cannot be reduced much further. However, the actual bit size is much larger than the theoretical limit of 10³ particles, and the storage capacity of the magnetic drives can be significantly increased by addressing signal-to-noise ratio issues. Substantial reduction of media noise has been achieved in films with partial magnetic isolation of grains. Cosputtering of Cr, carbon, and SiO₂, which are immiscible with cobalt magnetic alloy in solid state, results in phase segregation producing a thin layer of nonmagnetic substance separating the grains and thereby preventing cooperative switching and the zigzag noise. While this approach has been shown to be successful for creating a silica buffer layer between magnetic domains, the grain size and the thickness of the SiO₂ interlayer remains irregular and difficult to regulate. There thus remains a need to permit a direct control on the magnetization coupling between neighboring magnetic particles in such applications.

It is therefore a more specific object of the invention to provide a magnetic media having increased environmental stability, signal-to-noise ratio and storage capacity.

SUMMARY OF THE INVENTION

These and other objects and advantages are achieved in thin films of mono- and

multilayers of nanoparticles wherein a material which is inert with respect to the property of interest is deposited as a shell around each individual nanoparticle to physically and electronically isolate neighboring nanoparticles. For this reason, or in order to tailor the behavior of the nanoparticles themselves, the nanoparticle surface is modified with other materials having different properties.

In the present invention the structures of core-shell nanoparticles are engineered *ex situ*, i.e., prior to their deposition upon a film substrate, so as to achieve a particle with a size on the order of 1-100 nm having a core of an inorganic material upon which a layer of a different inorganic or high molecular weight organic material is deposited to form a shell.

The nanoparticles thus formed are then assembled into thin films utilizing a layer-by-layer assembly technique. Layer-by-layer deposition of nanoparticles offers important advantages, since it can be performed under ambient conditions and can be easily implemented for automated processes. The driving force for layer-by-layer assembly (LBL) is the electrostatic attraction of positive and negative charges situated on the surface of inorganic colloids and polyelectrolytes. This technique produces dense films with compact packing of nanoparticles with a unique combination of the characteristic properties of organic and inorganic materials.

In this manner, inorganic nanoparticles of various nature (magnetic, metallic, semiconducting, etc.), in which the individual surface is homogeneously coated with a different inorganic or high molecular weight organic material, are utilized for the preparation of mono- and multi-layers, by means of the layer-by-layer assembly process upon various kinds of substrates (glass, quartz, plastics, etc.).

In one preferred aspect of the invention, layer-by-layer assembled films of silica coated monodomain magnetic nanoparticles are provided, which can be used for various magnetic devices. The thickness of the silica coating is used as a determining factor for the separation between magnetic particles in each of the monolayers deposited. This allows for the attainment of densities of information without the need to use magnetic materials with such a high coercivity. The coating of the magnetic particles is carried out prior to the deposition of the particles upon the film substrate. Once the particle surface has been coated with silica, layer-by-layer deposition is performed, which essentially

consists of the following steps: (1) immersion of the substrate in an aqueous solution of a polyelectrolyte; (2) washing with deionized water; (3) immersion in an aqueous dispersion of coated nanoparticles; and (4) final washing with deionized water. This process is repeated so many times as necessary, depending on the number of layers required in order to obtain the specific properties of the desired material. In each of the layers a compact packing is produced, where the particles are in mutual contact, but the magnetic domains stay separated from each other by means of their respective coatings. Comparing the magnetic properties of the films prepared in this fashion with particles whose only difference is the presence or absence of an isolating coating, it is observed in the films prepared with coated nanoparticles a decrease of the magnetic susceptibility, which is attributed to the reduction of exchange coupling between particles coated with silica, thus proving the utility of the proposed technique for the application of information storage.

The alternated placement of layers of components positively and negatively charged is the key principle of layer-by-layer self-assembly and is an important aspect of the present invention. Once deposited, each layer provides a surface "favorable" for the adsorption of the next one, assisted by electrostatic attraction. The presence of a considerable surface charge assures a practically monomolecular nature of the films due to the electrostatic repulsion between the just formed layer and free particles floating in solution. The thickness of the individual layers depends on the particle size and lies typically in the range between 3 and 50 nm. The consecutive deposition of polyelectrolyte and nanoparticle layers produces the typical alternate structure of these films. The use of nanoparticles formed previous to the assembly process allows for the abovementioned surface modification of the nanoparticles, previous to their organization into film, which makes possible the optimization of the individual particle properties and the isolation between adjacent particles.

Several features distinguish the layer-by-layer assembly of core-shell nanoparticles from traditional film deposition processes: (1) tolerance to substrate shape and size; (2) easy adaptation to film preparation on most of technologically important materials; (3) possibility to form organized layered structures from different materials; and (4) superb mechanical properties of coatings. Importantly, the assembly of pre-made

nanoparticles allows for both utilization of pre-made, structurally optimized nanoparticles and for facile control over the sequence of materials.

Simplicity and universality of the layer-by-layer assembly makes it technologically viable for the production of a variety of thin film nanostructured materials. Synthesis of aqueous dispersion of nanoparticles affords application of LBL to the preparation of hybrid organic-inorganic multilayer composites. Size dependence of nanoparticle properties and processability of polymers can be utilized to produce materials with a unique combination of mechanical, electrical, optical, and magnetic characteristics. Sequential absorption of inorganic colloids and oppositely charged polyelectrolytes has been demonstrated by others for semiconductor nanoparticles, metal nanoparticles, silica particles, and exfoliated layered compounds. These LBL multilayers display characteristics for the preparation of light-emitting diodes, resists, sensors, electrically conductive films, nonlinear optical devices, and gas separation membranes. It is thus proposed that the present invention has application in the preparation of light-emitting diodes from core-shell semiconductor nanoparticles; electrochromic films from coated metallic particles; sensors from coated semiconductor nanoparticles; magneto-optical devices from silica coated YIG nanoparticles; antireflective coatings from silica and polymer-coated nanoparticles; functional coatings of optical fibers, and others.

Among other compounds used for LBL, magnetic nanoparticles have received little attention so far and it is to this application that the preferred embodiment of the present invention is directed. As an alternative to traditional deposition techniques for preparation of magnetic films, such as sputtering and vacuum evaporation, layer-by-layer deposition of magnetic nanoparticles possesses important unique features: (1) LBL deposition can be performed at ambient conditions and does not require subsequent annealing of the deposited film. This permits preparation of magnetic coatings on a variety of inexpensive substrates such as glass, plastic, and aluminum. (2) Nanoparticles can be preselected according to their size and shape prior to the assembly. High grain size uniformity is an important factor for the further improvement of advanced magnetic storage media. (3) By using preformed nanoparticles, one gains a new level of control over the properties of the magnetic grains. Besides narrowing down the size distribution, methods of colloidal chemistry allow for the coating of individual magnetic grains with

different materials, which is compelling for the optimization of coercivity, the increase of saturation magnetization, and the decoupling of magnetization switching in adjacent nanoparticles. Utilization of *ex-situ* made nanoparticles opens the possibility for control and optimization of the domain size and shell thickness and for substantial improvement of size distribution.

Superparamagnetic Fe_3O_4 nanoclusters are provided as a model system in the preferred embodiment to demonstrate the formation of organic-inorganic sandwich films of magnetic nanoparticles and to establish the effect of silica coating on functional properties of magnetic thin films prepared by the LBL technique. The present invention provides formations of densely packed assemblies of Fe_3O_4 nanocrystallites with good adhesion to a variety of substrates and excellent mechanical characteristics. Importantly, in such assemblies, the exchange coupling across grain boundaries and cooperative switching in adjacent magnetic grains is found to be greatly impeded by the silication.

Heretofore, core-shell nanoparticles have been used as a conjugate to proteins for the purpose of serving as indicators or labels for chemical reactions.

A better understanding of the present invention, its several aspects, and its objects and advantages will become apparent to those skilled in the art from the following detailed description, taken in conjunction with the attached drawings, wherein there is shown and described the preferred embodiment of the invention, simply by way of illustration of the best mode contemplated for carrying out the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional representation of the inventive film of core-shell nanoparticles assembled by the layer by layer process as applied on a substrate (planar or otherwise).

FIG. 2 is an illustration of the main steps used in connection with the present invention for the coating of magnetic particles with silica shells.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Before explaining the present invention in detail, it is important to understand that the invention is not limited in its application to the details of the construction illustrated and the steps described herein. The invention is capable of other embodiments and of being practiced or carried out in a variety of ways. It is to be understood that the phraseology and terminology employed herein is for the purpose of description and not of limitation.

The preferred embodiment of the present invention encompasses the use of inorganic core particles of various nature, such as, for example, magnetic, metallic and semiconducting particles, whose individual surface is homogeneously coated with a shell of a different inorganic or high molecular weight organic material, for the preparation of mono- and multilayers by means of the layer-by-layer self-assembly technique upon various kinds of substrates, including but not limited to glass, quartz, plastics and other materials. The structures of the core-shell nanoparticles are engineered *ex situ*, i.e., prior to their deposition upon a film substrate, so that the property of interest of the nanoparticles is preserved and the individual nanoparticles are isolated with respect to each other and with respect to their exposure to the environment when assembled into a thin film. A polyelectrolyte layer is deposited between every nanoparticle layer as a part of the LBL deposition procedure.

The preparation of core-shell nanoparticles may be performed through different well-established methods, depending on the nature of the core and the shell materials. Most of the existing techniques for the homogenous deposition of a shell onto a core are based upon chemical methods in solution, often involving several differentiated steps, such as (1) the deposition of "active silica" (silicate solution at certain pH and concentration) from an aqueous solution, (2) hydrolysis and condensation of alkoxysilanes in ethanol, (3) successive reactions in microemulsions, (4) decomposition of organometallic precursors at high temperature, (5) injection of aqueous solutions of metal salts, (6) surface polymerization of latexes, and others.

More particularly, the process for the assembly of films of core shell nanoparticles, comprises the steps of:

preparation of aqueous dispersions of coated nanoparticles as
aforedescribed;

obtaining a suitable substrate;

cleaning the substrate to remove surface contaminants;

5 forming at least one layer of coated nanoparticles by the substeps of:

a.) immersion of the substrate in an aqueous solution of a polyelectrolyte
so as to apply one monolayer of the polyelectrolyte to the substrate;

b.) rinsing the substrate with deionized water;

c.) immersion of the substrate in the aqueous dispersion of coated
10 nanoparticles; and

d.) final washing with deionized water.

Additional layers of coated nanoparticles and polyelectrolyte to the substrate may
be sequentially applied so many times as necessary, depending on the number of layers
required to obtain the specific properties desired. In each of the layers a compact packing
15 is produced, where the property of interest of the particles are isolated by means of their
respective coatings. The thickness of the individual layers depends on the particle size
and lies typically in the range between 3 and 50 nm.

Referring now to the drawings, wherein like reference numerals designate
identical or corresponding parts throughout the several views, and, more specifically, to
20 FIG. 1, there is illustrated a thin film 10 constructed in accordance with the preferred
embodiment of the present invention. The inventive film 10 is formed on a substrate 12
which comprises a glass, quartz, plastic or other inert material. Individual nanoparticles
14, each consisting of a core 16 of a first inorganic material and a shell 18 of a second
inorganic or high molecular weight material, are arranged by virtue of the LBL assembly
25 process in layers separated by polyelectrolyte 20. The shell 18 for most applications may
be made of metal oxides or polymers. As used herein, a "high molecular weight"
material refers to polymers, including proteins, having a molecular weight greater than
about 1000 atomic units.

It is particularly preferred to construct thin films of magnetic media wherein
30 magnetic nanoparticles of various nature (magnetite and other ferrites, yttrium iron garnet
(YIG), cobalt, iron, etc.), whose individual surface is homogeneously coated with an

inorganic insulating material, such as silica, are formed in mono- and multilayer thin films by means of LBL self-assembly upon various inert substrates. The thickness of the coating is used to isolate each magnetic particle in each of the monolayers deposited.

The initial coating of the magnetic particles is preferably carried out in solution in a two stage process, and reference is now made to FIG. 2 in this regard. In the first stage, the magnetic particles 16 are dispersed in a silicate solution, such as a sodium silicate solution, so that the silica oligomers present form initial bonds on the oxide surface of the particles. In the case of some materials, such as metals like cobalt and iron, it is necessary to use a coupling agent, which are well known, to make the particle surface receptive to the bonding of silane moities. Once this initial bond is formed, the second stage is performed which consists of the addition of a solvent in which the silica is practically insoluble, such as ethanol. This produces the precipitation of silicate groups preferentially on the magnetic particles present in solution, which act as nuclei for subsequent growth. The amount of silicate present, as well as pH of the solution, determine the thickness of the silica shell deposited on the magnetic nuclei. In the case that the thickness is to be increased further, one can proceed with the addition of tetraethoxysilane ($\text{Si}(\text{OCH}_3)_4$) and ammonium hydroxide (NH_4OH) whereby the hydrolysis of the silane gives place to additional silica condensation on the particles initially coated.

Once the magnetic particles have been coated with silica, LBL assembly is performed as aforescribed to construct thin films of magnetic media.

As thus explained, in accordance with the invention layered magnetic materials prepared by LBL offer a significant alternative for the design of magnetic coatings. One of the principal advantages as compared to sputtering, pulse laser deposition, and similar methods, is the opportunity to engineer the structure of individual magnetic grains while being simple in realization. This is demonstrated by using a model system of superparamagnetic Fe_3O_4 nanoparticles, and the present invention will be further understood with reference to the following non-limiting examples. Identical films of pristine and silica-coated nanoclusters are assembled in organic-inorganic sandwich films with good mechanical properties. Magnetic measurements reveal drastic reduction of the cooperative magnetization switching between adjacent nanoparticles due to the presence

of the insulating silica shell. Provided the coercivity of the particles is increased to 1.5-2.5 kOe, LBL assembly of silica coated nanoparticles may be considered for the design of low-noise high-density magnetic media.

EXAMPLE 1

5 Silicon wafers (Virginia Semiconductors) were used as received. Microscope cover glass slides were cut in ca. 0.7×1.5 cm pieces and etched by Ar plasma for 30 seconds in a Denton Desktop II magnetron sputterer/etcher at 120 mTorr of Ar to remove surface contaminants. A commercial 20% aqueous solution of poly(dimethyldiallylammonium bromide), PDDA, (Aldrich) was diluted 20 times to
10 obtain a 1% solution which was used for film preparation. FeSO_4 , FeCl_3 , HCl, NH_4OH , tetramethylammonium hydroxide (all Aldrich), sodium silicate solution (27 wt% SiO_2 , Aldrich), and pure grade ethanol were used as received. Milli-Q deionized water (18 M Ω) was used for all the preparations.

Aqueous dispersions of magnetite nanoparticles were prepared according to the
15 procedure published by Correa-Duarte, M.A.; Giersig, M.; Kotov, N.A.; Liz-Marzan, L.M. in *Langmuir*, 1998, 14, 6430-6435, said publication being incorporated by reference herein. Briefly, 20 mL of FeCl_3 (1M) and 5 mL of FeSO_4 (2M) in 2M HCl were added to 250 mL of NH_4OH (0.7 M) under rapid mechanical stirring, which was allowed to continue for 30 minutes. The black solid product was decanted with the help of a
20 magnet. The sediment was then redispersed in 50 mL of distilled water, and subsequently three aliquots of 10 mL tetramethylammonium hydroxide solution (1M) were added, again with rapid stirring. Finally, water was added to the dispersion up to a total volume of 250 mL. In this way a stable dispersion of crystalline, approximately spherical magnetite nanoparticles are obtained with an average diameter of 12 nm.

25 In order to homogeneously coat the particles with silica, 4 mL of the resulting aqueous magnetite dispersion was further diluted up to 100 mL, and then 4 mL of 0.54 wt% sodium silicate solution at pH = 10.5 was added under stirring. The pH was then adjusted to 10 with HCl (1M), and the colloid was stirred for about 2 hours and allowed to stand for 4 days. Examination of the coated particles so obtained with a transmission
30 electron microscope reveals that each initial crystalline Fe_3O_4 particle is coated with an average thickness of some 5 nm. As mentioned above, it is possible to vary the thickness

of the silica shell by means of transfer onto ethanol and addition of ammonium hydroxide and tetraethoxysilane in amounts specified in well known scientific literature.

5 The layer-by-layer assembly was performed according to the standard cyclic procedure: chemically cleaned glass or silicon wafer slides were sequentially exposed to solutions of poly(diallyldimethylammonium) chloride (PDDA) (1g/L) and coated or uncoated nanoparticles. Between these two steps, the substrates were thoroughly rinsed in three baths of deionized water with total duration of five minutes. Exposure times for solutions of PDDA and nanoparticles were two and five minutes respectively.

10 Atomic force microscopy images were taken by using a Nanoscope IIIa instrument operating in the tapping mode with silicon nitride tips. Typically, the surface was scanned at 2 Hz with 256 lines per image resolution and 1.2 - 4.0 V set-point.

Magnetic measurements were performed by using a Quantum Design PPMS 6000 magnetometer. The magnetic field H was created by a superconducting solenoid in the persistent mode parallel to the film's surface. The ac field with a peak-to-peak amplitude of 12 Oe and 987 Hz was applied along the dc magnetic field. The resulting ac susceptibility data are reported as in-phase, χ , and out-of-phase, χ' , signals. For the magnetic hysteresis loops, the correct dc magnetization values, M , corresponding to the sample signals were obtained by subtracting the diamagnetic signal of the substrate from the total registered signal. The linear magnetic response of silicon wafers was intrapolated inside the $-10 \text{ kOe} < H < 10 \text{ kOe}$ region from the high field $M(H)$ wings of the magnetization curve.

25 Conductivity measurements were performed by using a Keithley 6517 high-resistance meter capable of registering resistivities as high as $10^{17} \Omega$. Subsequent to the preparation of the LBL film on a 1 cm wide glass slide, two gold stripes 2 cm apart were sputtered on its surface in a Denton Desktop II magnetron sputterer. The slide was positioned in a carefully shielded cell made of grounded copper mesh. The contacts to the high-resistance meter were made by copper alligator connectors. The resistivity reading was allowed to stabilize for 5 minutes to account for slight variations in temperature and humidity. The measurements were repeated at least three times with each slide.

30 TEM images were taken in a Phillips CM-12 instrument operating at an

acceleration voltage of 120 kV, equipped with a high resolution lens and 9800 EDAX analyzer. High resolution images were digitally recorded with a CCD camera.

Transmission electron microscopy images revealed the formation of continuous and uniform silica coating on magnetite nanoparticles. A SiO₂ shell was seen for every individual particle with a thickness varying within ca. 25%. Its average value can be controlled by the duration of the hydrolysis from a monolayer to several core diameters.

The procedures of the preparation of sandwich layers of "naked" and silica-coated nanoparticles are virtually identical. The minimal disturbance to the film structure is essential when comparing the magnetic interactions between the particles. The total number of nanoparticles deposited in each cycle is found to be dependent on the pH of the dispersion, which reflects the difference in the point of zero charge for Fe₃O₄ and SiO₂. The adjustment of this parameter within one pH unit permits attaining the equality of the surface density of coated and uncoated magnetite nanoparticles deposited in one LBL cycle. For the first ten layers, the increase of optical absorption in the region corresponding to the band gap of magnetite follows a similar, almost linear dependence for both Fe₃O₄ and Fe₃O₄/SiO₂. For commercially available GMR reading heads, the operational thickness of magnetic material can be as small as few nm, which corresponds to a monolayer of nanoparticles.

Prepared nanostructured films demonstrate exceptional adhesion to the substrate (glass, Si wafers, etc.). The test of mechanical characteristics has been done for magnetite/PDDA multilayers assembled on thin poly(ethyleneterephthalate) film (Mylar™) in order to increase the level of mechanical strain. The thin flexible substrate carrying a ten layer LBL film on it, has been subjected to intense physical stress as described in Kotov, N.A.; Magonov, S.; Tropsha, E. *Chem. Mater.* 1998, 10, 886-895. No peeling or crack formation was seen when surveying the surface of magnetite/PDDA films by optical or atomic force microscopy. For any kind of substrate, no change in appearance and physical integrity of the films can be observed for more than a year since they were deposited.

AFM images of LBL films on silica wafers indicate that prepared colloidal dispersion produce films with high surface density of nanoparticles, and most of them are in physical contact with each other. It is important that besides a thin adsorption layer of

tetramethylammonium and hydroxide ions, no other organic substances such as long chain surfactants or polymers, be used to stabilize and assemble magnetic particles. Thick organic coating or polymeric stabilizer such as polyacrylic acid, can impede the observation of short-range exchange interactions between magnetic particles.

5 On the topography scans both for Fe_3O_4 and $\text{Fe}_3\text{O}_4/\text{SiO}_2$, one can see clusters of nanoparticles. Their formation is attributed to the agglomeration of inorganic colloid on partially detached segments of the polyelectrolyte protruding into the bulk solution. Greater mass of silica coated magnetite amplifies the tendency of the nanoparticles to conglomerate. Although undesirable in most cases, in the framework of this example,
10 the tight agglomerates with small interparticle distances can be, in fact, beneficial because of closeness of magnetic cores.

Reversibility of the magnetization loops revealed that both coated and uncoated nanoparticles are mostly superparamagnetic in the range of temperatures from 2 to 300°K. Small splitting of ± 15 Oe observed between two peaks of magnetic susceptibility is likely
15 to be associated with the residual magnetic field unavoidably present in the superconducting solenoid when scanning in the range of ± 10000 Oe.

Saturation magnetization, M_s , for silica-coated magnetite is lower than for uncoated nanoparticles obtained after the same number of deposition cycles. Since UV-VIS absorption spectra indicate approximately equal, or even slightly greater amount of
20 $\text{Fe}_3\text{O}_4/\text{SiO}_2$ in a 10 layer LBL film than for uncoated magnetite, the decrease of M_s should be attributed to intrinsic properties of the nanoparticle surface. For core-shell nanostructures, a similar reduction of M_s has been recently reported for cobalt and iron-based magnetic systems. See Chen, J.P.; Sorensen, C.M.; Klabunde, K.J.; Hadjipanayis, G.C. *Phys. Rev. B* 1995, 51, 11527-11532 and Easom, K.A.; Klabunde, K.J.; Sorensen,
25 C.M.; Hadjipanayis, G. *Polyhedron* 1994, 13, 1197-1223. A surface enhanced magnetic moment originating in the transition of interfacial *d*-metal atoms to a high-spin state, is likely to be responsible for this effect. Surface magnetism was theoretically predicted as well as experimentally observed for various thin magnetic layers (Himpsel, F.J.; Ortega, J.E.; Mankey, G.J.; Willis, R.F. *Advances in Physics* 1998, 47, 511-597) as well as for
30 naked nanoparticles (Kodama, R.N.; Makhlof, S.A.; Berkowitz, A.E. *Phys. Rev. Lett.* 1997, 79, 1393). Silica coating is likely to relax the stress and eliminate poorly

coordinated bonds of surface iron atoms, which reduces the total spin and decreases the magnetic moment of nanoparticles in the LBL assembly.

The temperature dependence of in-phase and out-of-phase magnetic susceptibility -- χ and χ' respectively -- provides additional piece of information on magnetic properties of LBL assemblies. In the low temperature limit, the peak value of magnetic losses is proportional to the characteristic time scale of magnetic moment reversal:

$$\chi''(T) \sim (KV/k_B T)^{1/2} \exp(-KV/k_B T),$$

where k_B is the Boltzmann constant, T is temperature, K is the magnetic anisotropy constant, and V is the volume of the nanoparticles. In the case of SiO_2 -coated species, the K parameter, obtained from the best fit of this equation to the temperature dependence, yields the anisotropy constant of bulk Fe_3O_4 that is $K = 1.1 \cdot 10^5 \text{ erg/cm}^3$. Interestingly, for naked nanoparticles, K exceeds the bulk value by 3 times. The good correlation between K values for bulk magnetite and silicated nanoparticles confirms relaxation of surface states of iron when bound to SiO_2 . However, such a significant difference in K between coated and naked nanoparticles most likely implies the combined effect of the surface enhanced magnetism and interparticle interactions. Interdependence of these two factors can also be seen in an abrupt drop in χ' above 200°C , which indicates a qualitative change in the magnetization reversal mechanism at relatively high temperatures.

Magnetic interactions between nanoparticles in the LBL film can be assessed from the χ vs. H data. A trace for $\text{Fe}_3\text{O}_4/\text{SiO}_2$ showed that χ in this example is reduced by a factor of 10 as compared to uncoated magnetite. As was also seen, χ' decreases approximately proportionally to χ . Since neither variations in packing, nor in the amount of the inorganic material in the prepared LBL films are significant, the change in χ and χ' should be attributed to the insulating effect of the silica shell. The thin layer of SiO_2 produces an electron tunneling barrier between the semiconducting/magnetite cores. This weakens interparticle exchange interactions, facilitated for naked magnetite owing to their immediate physical contact. Magnetic dipole coupling can still be present between the particles because of the long-range nature of these forces.

The transfer of spin-polarized electrons promotes the magnetization switching of adjacent magnetic grains thereby increasing the overall susceptibility of the sample. The disruption of the electronic communication between nanoparticles eliminates cooperative

magnetization switching which often occurs similarly to a falling domino, when magnetic reversal of one particle induces reorientation of the magnetic moment in numerous grains coupled to each other. This results in a reduction of all components of magnetic susceptibility and the corresponding decrease of noise. According to the fluctuation-dissipation theorem, the noise intensity is proportional to the out-of-phase component of the ac susceptibility.

Though surface enhanced magnetism in naked nanoparticles may be partially responsible for the reduction in susceptibility of coated ones, it cannot fully account for it since the reduction in χ and χ' is five times stronger than the decrease in M_s .

The interference of the silica coating with the interparticle electron exchange can be confirmed by conductivity measurements. The resistivity measured laterally between two gold electrodes is found to be $30 \pm 5 \text{ G}\Omega$ when bridged by a ten-layer LBL film of naked magnetite. An identical assembly of silica-coated magnetic nanoparticles with the same number of layers and the same optical density yields resistivity values of at least two orders of magnitude higher, which clearly shows retardation of the electronic communication between nanoparticles.

EXAMPLE 2

Yttrium iron garnet (YIG) particles were obtained commercially from Nanomaterials Research Corporation (Longmont, Colorado). The diameter of these spherical particles lies between 10 nm and 60 nm. The particles were obtained in the form of a powder, and it was necessary to disperse them in water previous to the coating process. This redispersion is performed by adding 0.1 g of the powder on 10 mL of a sodium silicate aqueous solution with a concentration adjusted so that the pH is within the range 11-12, the introduction occurring in an ultrasonic bath for 4 hours. After that period, 2.5 mL of the obtained dispersion is diluted inside the same ultrasonic bath with distilled water up to a total volume of 40 mL. Finally, 160 mL of ethanol are added, so that the precipitation of the silicate still in solution takes place, mainly on the magnetic particles. The process of thin film assembly is the same as that specified in the previous example for magnetite nanoparticles.

* * * * *

While the invention has been described with a certain degree of particularity, it is manifest that many changes may be made in the details of the process of assembly without departing from the spirit and scope of this disclosure. It is understood that the invention is not limited to the experimental methods set forth herein for purposes of
5 exemplification, but is to be limited only by the scope of the attached claim or claims, including the full range of equivalency to which each element or step thereof is entitled.

WHAT IS CLAIMED IS:

1. A process for the assembly of films of core-shell nanoparticles, comprising the steps of:

preparing an aqueous dispersion of coated nanoparticles, each nanoparticle having a core made of a first inorganic material and a shell made of a second inorganic or a high molecular weight organic material;

subsequent to the prior step, forming at least one layer of said coated nanoparticles upon a substrate by the substeps of:

- a.) exposing said substrate to said aqueous solution of a polyelectrolyte to establish a first charge upon said substrate;
- b.) rinsing said substrate with deionized water;
- c.) exposing said substrate to said aqueous dispersion of said coated nanoparticles, said nanoparticles possessing a charge opposite said first charge, whereby the electrostatic attraction of said coated nanoparticles to said first charge results in the formation of a layer of said coated nanoparticles upon said substrate; and
- d.) rinsing said substrate with deionized water.

2. The process according to claim 1 further comprising sequentially applying additional layers of said polyelectrolyte and said coated nanoparticles to said substrate to create a multilayered film thereon.

3. The process according to claim 1 wherein said core comprises a magnetic material.

4. The process according to claim 3 wherein said core comprises magnetite.

5. The process according to claim 3 wherein said shell comprises silica.

6. The process according to claim 1 wherein said polyelectrolyte is poly(diallyldimethylammonium)chloride.

7. A film formed on a substrate, comprising at least one layer of individual nanoparticles, each said nanoparticle consisting of a core made of a first inorganic material and a shell made of a second inorganic or a high molecular weight organic material, said substrate having a surface modified by a polyelectrolyte to possess a first charge, said coated nanoparticles possessing a charge opposite said first charge, whereby the electrostatic attraction of said coated nanoparticles to said first charge results in the formation of a layer of said coated nanoparticles upon said substrate.

8. The film according to claim 7 wherein the thickness of said layer is between 3 and 50 nm.

9. The film according to claim 7 further comprising a plurality of layers of said coated nanoparticles, each layer separated by a polyelectrolyte layer.

10. The film according to claim 7 wherein said core comprises a magnetic material.

11. The film according to claim 10 wherein said core comprises magnetite.

12. The film according to claim 10 wherein said shell comprises silica.

13. The film according to claim 7 wherein said polyelectrolyte is poly(diallyldimethylammonium)chloride.

14. The film according to claim 7 wherein said substrate comprises glass.

15. The film according to claim 7 wherein said substrate is planar.

16. The film according to claim 7 wherein said film further comprises an optical, magnetic, electrical, catalytic or biologically active coating.

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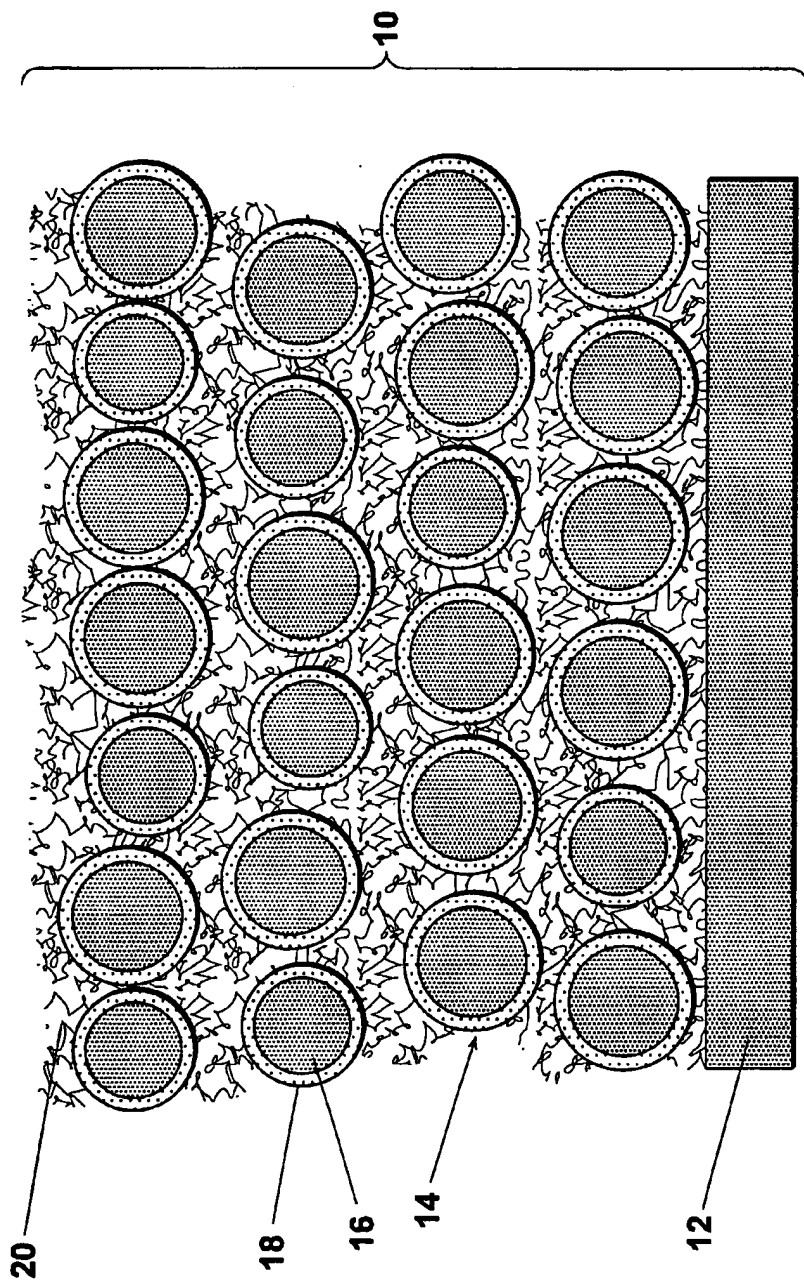


Fig. 1

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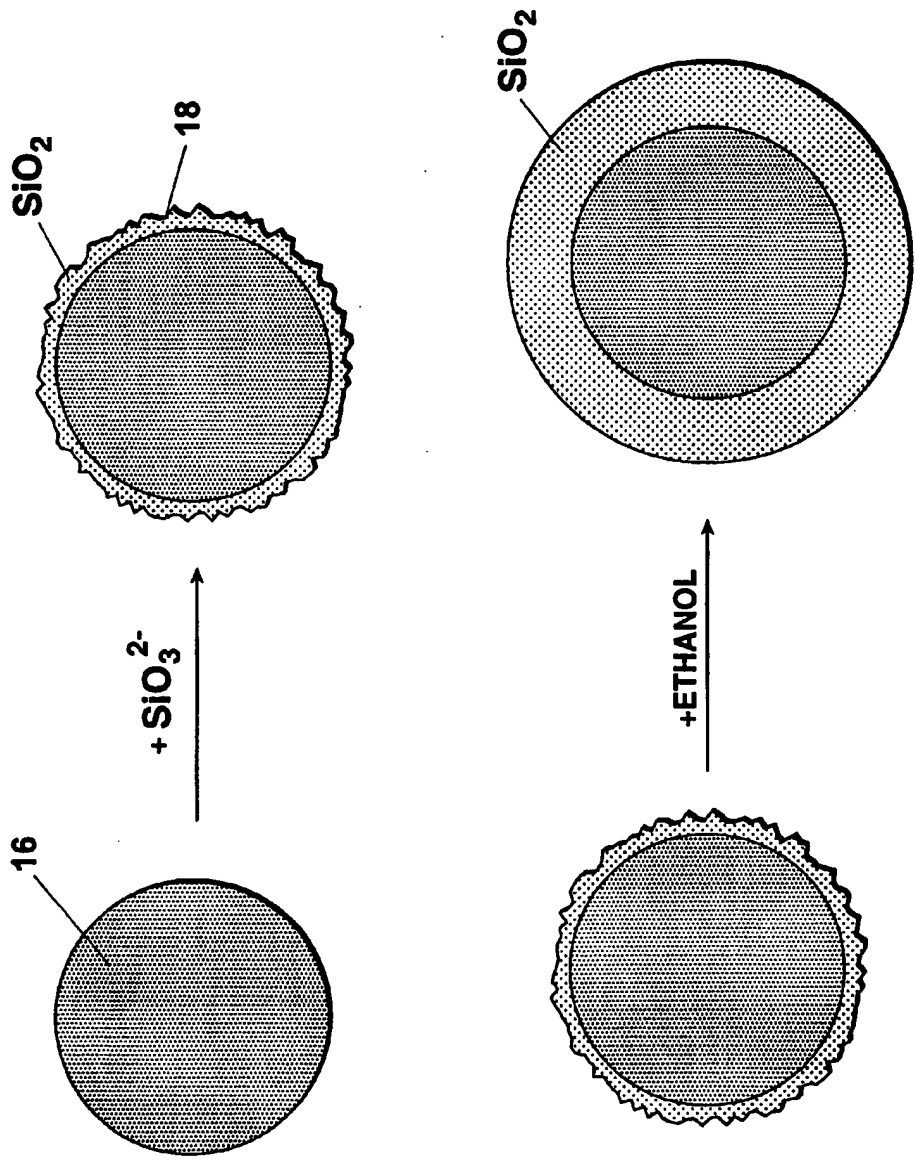


Fig. 2

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/US 00/02358

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B05D1/14 B05D3/00 G11B5/62

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B05D G11B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 203 205 A (IBM DEUTSCHLAND ; IBM (US)) 3 December 1986 (1986-12-03)	1-5, 7, 8, 10-16
Y	claims 1, 2, 6, 7, 9 page 9, line 13 - page 14, line 8; figure 3	1-5, 7, 8, 10-16
Y	EP 0 101 826 A (IBM) 7 March 1984 (1984-03-07) claim 1	1-5, 7, 8, 10-16

☐ Further documents are listed in the continuation of box C.


Patent family members are listed in annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

20 June 2000

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 00/02358

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